METHIDATHION

RISK CHARACTERIZATION DOCUMENT

Volume III

ENVIRONMENTAL FATE

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By

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ENVIRONMENTAL FATE OF METHIDATHION

- **Chemical Description**

Chemical Name (CA)	S-[(5-methoxy-2oxo-1,3 4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl phosphoro-dithioate
Common Name	Methidathion
CAS Registry Number	950-37-8
Molecular Formula	$C_6H_{11}N_2O_4PS_3$
Molecular Weight	302.33
Chemical Family	Organophosphorus; thiadizole

Methidathion is a colorless crystal belonging to the chemical family of organophosphates (sub-class phosphorodithioates). It is sparingly soluble in water and readily soluble in common organic solvents such as ethanol, benzene, methanol, and acetone. Methidathion is hydrolyzed in alkaline and strongly acidic media, and is relatively stable to hydrolysis in neutral and slightly acidic media (British Crop Protection Council. 2003; O'Neil, 2001). Additional physical and chemical properties are summarized in Table 1. Wildlife toxicity data are summarized in Table 2.

Table 1.   Physical and chemical properties of methidathion (DPR, 2005a; British Crop Protection Council, 2003).

Physical/Chemical Property	Value
Melting point	39.9 °C
Vapor Pressure	3.37×10^{-6} mm Hg (25 °C)
Water Solubility	221 ppm (22 °C, pH 4.4)
Henry's Law Constant (K_h)	1.95×10^{-9} atm-m^3-mol
Octanol-water Partition Coefficient (K_{ow})	166

Table 2.   Wildlife toxicity of methidathion (Menconi & Siepmann, 1996; U.S. Environmental Protection Agency, 1999).

Species	Test	Toxicity
Mallard duck	14-day LD_{50}	23.6 mg/kg
Rainbow trout	96-hour LC_{50}	10.5 μg/L
Bluegill sunfish	96-hour LC_{50}	17.2 μg/L
Honeybee	48-hour LD_{50}	0.23 μg/bee
Mysid shrimp	96-hour LC_{50}	0.7 μg/L
Daphnia magna	48-hour LC_{50}	7.2 μg/L

- **Regulation**

Methidathion has been classified as a federally restricted use pesticide due to its high acute oral toxicity (U.S. Environmental Protection Agency, 1999). As per the Food & Agriculture Code, section 14004.5, the Director, DPR was authorized to list certain pesticides as Restricted Use Pesticides due to their adverse effects on people, animals and the environment. Consequently, it was designated a restricted material pursuant to section 6400 of the Food and Agricultural Code. Other criteria for a restricted material designation in this section include posing a danger to public health, or a hazard to crops, domestic animals, farm workers, or the environment. Restricted materials are possessed and used by persons only under permit of the county agricultural commissioner.

The Birth Defect Prevention Act (Stats. 1984, Ch. 669, § 1) mandates the listing of methidathion in section 13127.(a) of Title 3, California Code of Regulations. The 200 priority pesticide active ingredients listed in this section are suspected of being hazardous to people, and have widespread use and significant data gaps. All data requirements for methidathion have been submitted to the Department of Pesticide Regulation (DPR).

- **Use Profile**

Methidathion is a non-systemic insecticide/acaricide used to control sucking and chewing insects for a wide variety of crops. It is available in emulsifiable concentrate and soluble powder formulations, which have the signal word "Danger/Poison" on the product labels. It is also available in a soluble powder formulation, which has the signal word "Warning" on the product label. As of July 26, 2006, there were two active registrations for products containing methidathion (DPR, 2005b).

Methidathion is applied by aerial or calibrated power-operated ground spray equipment. Application rates are summarized in Table 3.

Table 3:　　　　Summary of methidathion application rates in pounds of active ingredient per acre.

Commodity	[a]Rates
Almonds; Deciduous Fruits	0.75 – 3
Artichokes	1.0
Citrus Fruits	5.0
Cotton	0.25 – 1.0
Mangoes	0.25 – 0.5
Olives	2.0
Safflowers; Sunflowers	0.5
Walnuts	1.0 – 2.0

[a] concentrated sprays

Full pesticide use reporting in California was implemented by DPR in 1990. All agricultural use must be reported monthly to the county agricultural commissioners. The county agricultural commissioners forward these data to DPR, who annually compiles and makes available a pesticide use report. Agricultural use is defined as including applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way. Although use in structural pest control is excluded from the definition, the use of pesticides designated as restricted materials pursuant to section 14004.5 of the Food and Agricultural Code must be reported. For non-agricultural applications, detailed information such as base meridian/township/range/section is not provided.

Figure 1 is a graphical representation of total pounds of methidathion used in California in 1991 and from 1994 through 2005. Total use ranged from 370,087 pounds in 1994 to 48,196 pounds in 2005. The average annual use for the twelve-year reporting period was 174,651 pounds. Table 4 and Figure 2 show use by county in 1991 and from 1994 through 2005 for counties where ten-year average use exceeded 60,000 pounds. Table 5 and Figure 3 show monthly use in 1991 and from 1994 through 2005. Table 6 and Figure 4 show methidathion use by commodity/site in 1991 and from 1994 through 2005 for

commodities where twelve-year total use exceeded 100,000 pounds (DPR PUR Database).

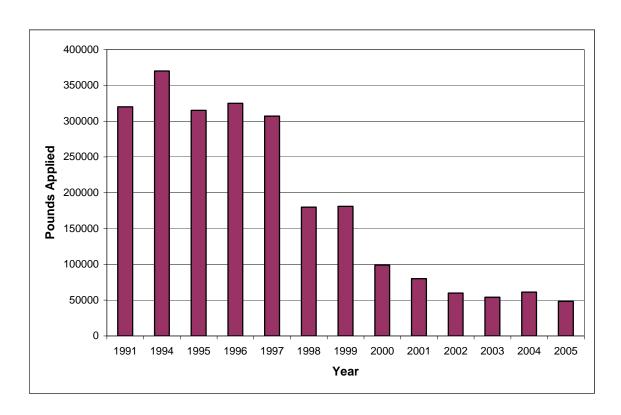Figure 1.   Methidathion reported use in 1991 and from 1994 through 2005 (DPR PUR Database).

Table 4.　　Methidathion use by county in 1991 and from 1994 through 2005 for counties where twelve-year total use exceeded 60,000 pounds (DPR PUR Database).
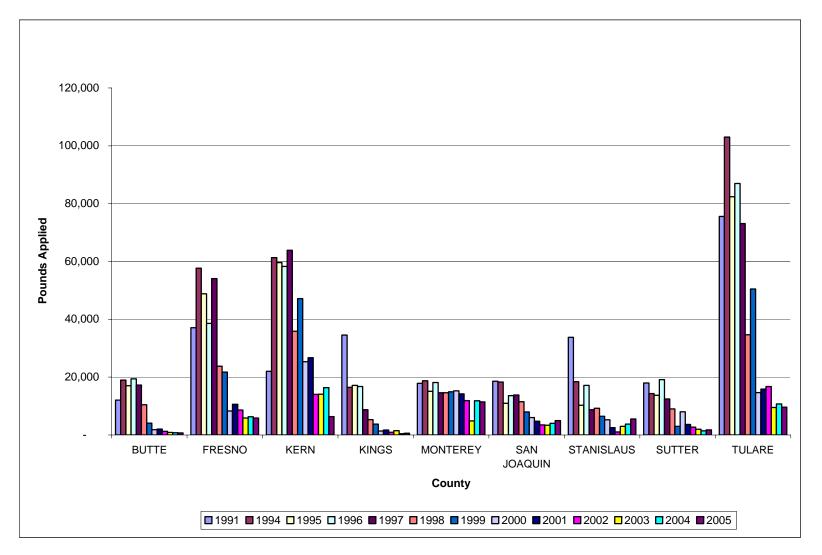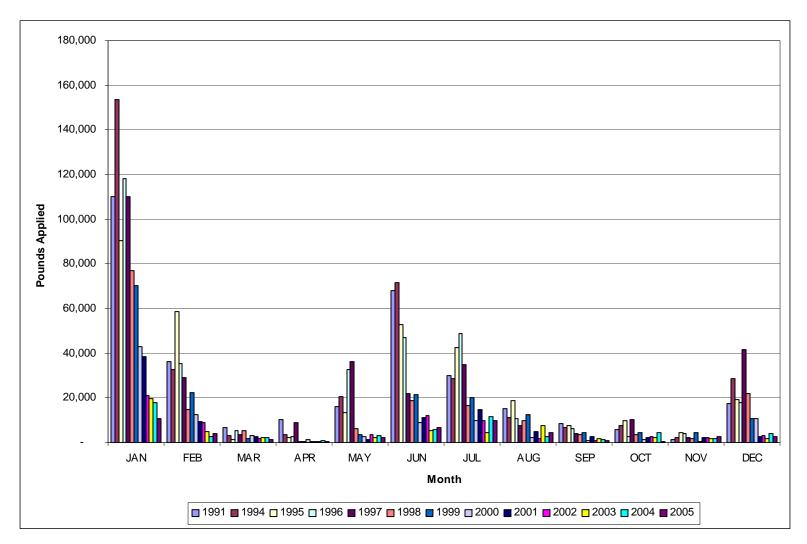
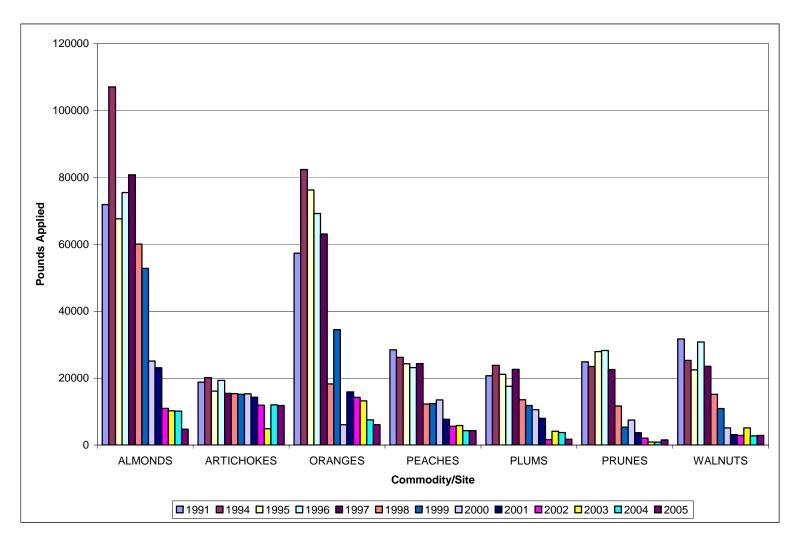| County	Pounds Applied												
	1991	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
BUTTE	12,029	18,973	17,041	19,417	17,232	10,451	4,105	1,845	2,060	1,245	875	758	698
FRESNO	37,117	57,658	48,841	38,599	54,073	23,773	21,740	8,305	10,611	8,628	5,881	6,277	5,881
KERN	21,994	61,333	59,625	58,300	63,855	35,901	47,145	25,340	26,722	14,048	14,128	16,355	6,371
KINGS	34,557	16,456	17,159	16,729	8,725	5,313	3,757	1,405	1,710	955	1,488	427	635
MONTEREY	17,867	18,743	15,070	18,147	14,581	14,581	14,950	15,271	14,220	11,903	4,851	11,823	11,473
SAN JOAQUIN	18,588	18,321	10,931	13,597	13,830	11,499	7,988	6,023	4,743	3,489	3,374	4,027	4,998
STANISLAUS	33,797	18,428	10,284	17,167	8,743	9,236	6,474	5,274	2,557	1,075	2,973	3,748	5,534
SUTTER	17,954	14,296	13,702	19,150	12,444	9,034	2,981	8,012	3,675	2,704	1,969	1,447	1,767
TULARE	75,582	103,008	82,379	86,966	73,097	34,695	50,483	14,630	15,857	16,736	9,518	10,753	9,635

Figure 2.   Methidation use by county in 1991 and from 1994 through 2005 for counties where twelve year total use exceeded 60,000 pounds (DPR PUR Database).

Table 5.   Methidathion use by month in 1991 and from 1994 through 2005 (DPR PUR Database).

Month	Pounds Applied												
	1991	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
JAN	109,978	153,786	90,534	118,038	110,277	76,851	70,346	43,098	38,718	21,024	19,816	18,097	10,523
FEB	36,301	32,723	58,792	35,331	28,978	14,580	22,314	12,418	9,269	8,990	4,934	2,716	3,871
MAR	6,687	3,347	1,343	5,541	3,434	5,266	1,951	3,332	2,757	1,953	2,142	2,246	1,141
APR	10,434	3,419	2,074	2,588	8,923	317	628	1,416	466	342	383	765	662
MAY	16,318	20,592	13,558	32,686	36,246	6,136	3,679	2,722	1,388	3,621	2,194	3,094	2,282
JUN	68,032	71,455	53,025	47,111	21,851	18,945	21,505	9,066	11,046	11,915	5,338	5,732	6,625
JUL	30,172	28,441	42,404	48,690	34,901	16,624	20,096	10,028	14,613	9,710	4,360	11,582	9,848
AUG	15,126	11,045	18,896	10,896	7,605	9,785	12,394	2,448	4,940	1,910	7,705	2,849	4,699
SEP	8,424	6,567	7,604	6,480	4,215	3,384	4,410	870	2,889	962	2,008	1,407	1,078
OCT	5,686	7,618	9,669	2,702	10,123	3,432	4,407	1,241	2,224	2,673	2,307	4,381	324
NOV	1,391	2,300	4,430	3,938	2,246	1,688	4,651	620	2,436	2,316	1,741	1,930	2,669
DEC	17,630	28,795	19,421	17,783	41,673	21,742	10,693	10,870	2,776	2,972	1,749	3,924	2,551

Figure 3.   Methidathion use by month in 1991 and from 1994 through 2005 (DPR PUR Database).

Table 6.   Methidathion use by commodity/site in 1991 and from 1994 through 2005 for commodities where twelve-year total use exceeded 100,000 pounds (DPR PUR Database).
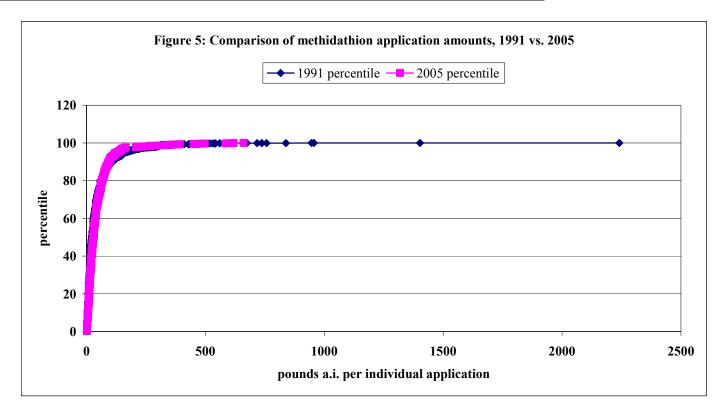
Commodity/Site	Pounds Applied												
	1991	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
ALMOND	71907	107060	67645	75516	80791	60115	52820	25120	23105	10974	10216	10126	4728
ARTICHOKES	18825	20130	16146	19325	15460	15336	15169	15331	14285	11920	4871	12010	11834
ORANGES	57362	82407	76283	69256	63123	18279	34480	6083	15909	14243	13200	7528	6088
PEACHES	28450	26201	24320	23178	24364	12225	12387	13504	7724	5605	5823	4314	4283
PLUMS	20736	23823	21142	17582	22643	13549	11838	10568	7981	1635	4136	3751	1722
PRUNES	24863	23484	27950	28263	22600	11655	5381	7454	3668	2073	912	867	1546
WALNUTS	31741	25315	22503	30812	23526	15162	10899	5130	3115	2879	5138	2751	2852

Figure 4.   Methidathion use by commodity/site in 1991 and from 1994 through 2005 for commodities where twelve-year total use exceeded 100,000 pounds (DPR PUR Database).

From the Figure 5 it is evident that methidathion application amounts during 1991 were little higher to that of 2005. In 1991 there were larger number of high pound applications relative to 2005. The table below summaries three percentile statistics and the corresponding methidathion pounds applied in 1991 and 2005.

Percentile	Pounds used in 1991	Pounds used in 2005
50	23.3	28.5
90	107.6	94.4
95	160.6	128.0

Figure 5: Comparison of methidathion application amounts, 1991 vs. 2005

From the Figure 6 it is evident that methidathion applied farm sizes during 1991 were larger to that of 2005, and in 1991 the total land area receiving methidathion was much higher. The table below summaries three percentile statistics and the corresponding methidathion applied acres in 1991 and 2005.

Percentile	Acres applied 1991	Acres applied 2005
50	18	20.1
90	88	80
95	150	100

Figure 6: Methidathion use acres 1991 vs 2005
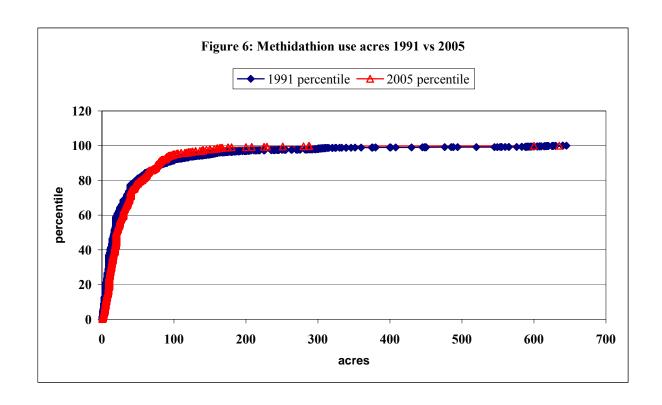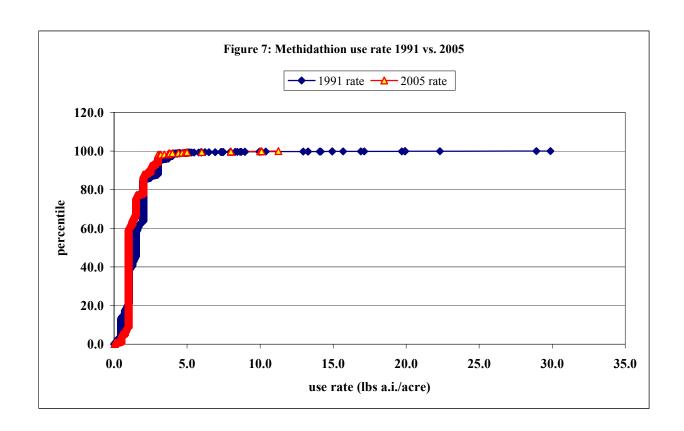
Figure 7 shows that methidathion use rates during 1991 were somewhat higher than that of 2005. Table below summaries three percentile statistics and the corresponding methidathion use rates in 1991 and 2005.

Percentile	Rate in 1991	Rate in 2005
50	1.49	1.0
90	2.99	2.5
95	3.09	3.0

Figure 7: Methidathion use rate 1991 vs. 2005

Fate and Persistence in the Aquatic Environment

The degradation rate of methidation in aquatic environment is reported to be influenced by factors such as temperature, and pH. Methidathion at a concentration of 10 mg/cm^3 were hydrolyzed in mediums with 0.1N HCl, and solutions buffered at pH values; 5, 7, 9, and 10 respectively and the concentrations of methidathion after hydrolysis were determined (Burkhard, 1978). Using these concentration values, rate constant (k $_{rate}$) values were calculated using the following relationship.

k $_{rate}$ = (ln c$_0$ – ln c)/ t.

   where c$_0$ = initial concentration
     c = concentration at time t
     k$_{rate}$ = rate constant in sec^{-1}

These k $_{rate}$ values were used to estimate the half-lives at given pH values and temperatures for that concentration of methidathion using the following relationship.

t $_{0.5}$ = ln 2 / 3600 x k $_{rate}$

   where 3600 is a conversion factor (1 hour = 3600 seconds).
   t $_{0.5}$ = half-life in hours

The values reported in Table 7 are some of the half-life estimates of methidathion using these relationships.

Table 7.   Methidathion hydrolysis half-lives (Burkhard, 1978).

Half-life, days	Temperature, °C	pH
41.3	20	1
10.0	30	1
0.8	50	1
0.08	70	1
33.8	20	5
9.0	30	5
0.63	50	5
0.08	70	5
40.8	20	7
10.1	30	7
0.83	50	7
0.09	70	7
25.5	15	9
12.3	20	9
3.1	30	9
0.25	50	9
2.8	15	10
1.9	20	10
0.54	30	10
0.05	50	10

In acidic conditions, hydrolytic cleavage occurred primarily at the C-S bond. Under alkaline conditions, cleavage occurred at the P-S bond. Both intermediate hydrolysis products; the 4-(hydroxymethyl)- and the 4-(mercaptomethyl)-2-methoxy-1,3,4-thiadiazole-5(4H)-one, were unstable and decomposed rapidly to yield 2 methoxy-1,3,4-thiadiazole-5(4H)-one, the major degradate, in the alkaline as well as acidic hydrolysis of

methidathion. In alkaline conditions, small amounts of a thioformic acid derivative were isolated. Given below is a schematic presentation of this process.

4(hydroxymethyl)-2-methoxy -1,3-4-thiadizole-5(4H)-one

4(mercaptomethyl)-2-methoxy -1,3-4-thiadizole-5(4H)-one

2 methoxy-1,3-4-thiadizole- 5(4H)-one

thioformic acid derivative

An aqueous photolysis study was conducted in distilled water at 25 °C using a mercury arc rated at 1900 $Jm^{-2}s^{-1}$ at a distance of 1.3 cm as the light source (Suter, 1983). The primary photodegradate was 2-methoxy-1,3,4-thiadiazole-5(4H)-one. The photolysis half-life was 8.1 days. In another study, the aquatic photolysis half-life ($t_{0.5}$) was found

to be 11 days at pH 7.0, and hydrolysis half-life ($t_{0.5}$) to vary from 37 days at pH 5, 48 days at pH 7 and 13 days at pH 9 (US EPA, 1999).

Methidathion has a low water solubility of 240 -250 mg/l at 20 ^{0}C. This increases the potential for this pesticide to run-offsite, and into surface water, depending on the conditions and the environmental factors. Methidathion was detected in California surface water due to rain run-off from winter dormant spray. In a study on the distribution and mass loading of insecticides in San Joaquin River, California, Ross et al., (1999) detected methidathion at a concentration of 0.08µg/l in one out of 18 samples analyzed for this pesticide. Ganapathy et al**.,** (1997) detected methidathion in 4 out of 222 samples (ranging from 0.061 to 0.22 ppb) from four California rivers; Sacramento river in November, 1993, Merced river in June, 1994, and Salinas and Russian rivers in August, 1994. Nordmark et al**.,** in 1998, were able to detect methidathion in two sampling locations in the Sacramento river; 0.056 µg/l at Bryte, and 0.071 µg/l at Sutter Bypass, during the winter of 1996-1997. In 1996, Menconi and Siepmann reported the hazard assessment of the insecticide methidathion to aquatic organisms in the Sacramento-San Joaquin River System. In their study, the most acutely sensitive freshwater species tested was the cladoceran; *Ceriodalphina dubia* with a 96-h LC_{50} value of 2.2 µg/l. The most acutely sensitive saltwater species was mysid *Mysidopsis bahia* with a 96-h LC_{50} value of 0.7 µg/l. The lowest freshwater Maximum Acceptable Toxicant Concentration (MATC) was 0.83 µg/l for cladoceran *Daphnia magna*. The only available saltwater MATC was 0.04 µg/l for mysid *M. bahia*. Because of the lack of data, no Final Acute Values or Final Chronic Values were calculated to establish Water Quality Criteria for methidathion. From the reports it is evident that methidathion has been detected many times in Sacramento-San Joaquin River System. The highest concentration detected was 15.1 µg/l (Menconi and Siepmann., 1996). They cautioned that methidathion might present an acute and chronic hazard to aquatic organisms, particularly to sensitive aquatic invertebrate species such as cladocerans and mysid.

Fate and Persistence in Soil
The data summarized in Table 8 show the organic-carbon-water partition coefficients for methidathion estimated for different soils for a given organic matter content. These coefficient values show considerable variability. The data were available for Adsorption Coefficient (K_d), Soil type, and % Organic matter (OM). K_{OC} values were calculated by using the formula $K_{OC} = K_d/OC \times 100$ where $OC = OM/1.8$. However, the K_{OC} values for methidathion in different soil types suggest considerable leaching potential.

Table 8.   Adsorption coefficients for several soil types in California**:** (DPR, 2005a).

Soil type	[a]OC	K_{oc}
Loam	0.7	415.7
Clay	2.8	310
Sandy	0.5	30.8
Sandy Loam	0.8	816
Sandy Loam	1.2	131.7
[a] = percent organic matter content		

Johnson, 1991 reported some of the important characteristics of pesticides to be considered potential leachers or non-leachers. The K_{OC} values, water solubility, half-life in moist soils, organic matter content and composition, all can influence the final outcome. Clayton, 2005 reported Methidathion to be a potential leacher.
A study on field soil dissipation of methidathion applied to bare ground plots in Vero Beach, Florida, (DPR, 1986) to determine the stability and mobility in an Immokalee fine sand soil, the following was concluded. When this pesticide was applied at 4.0 lbs of active ingredient (a.i.) per acre, the detected methidathion concentrations in the 0-6" soil layer reached a maximum value of 1.6-1.8 ppm. The calculated first order half-life was 5 days. Methidathion residues were detected in 6-12" soil cores collected 0-7 days after application, and decreased to below the detection limit by 21 days after application. None was detected from any subsequent sampling depths. These results indicate that methidathion is not persistent in soil, and will not likely migrate below12" in the field. The information submitted by the registrant, (DPR 1995a) shows that the most significant degradation pathway for methidathion in the environment is via microbial processes in the soil. The half-life in the aerobic soil is approximately 3 days. Anaerobic soil metabolism is also relatively rapid with a reported half-life of 30 days. Methidathion and its metabolites have a low mobility in soils. The compound is rapidly degraded in soil and in water by chemical, photolytic, and biological processes.

Artificial sunlight photodegredation of ^{14}C-methidathion on a sandy loam soil collected in Tulare County, California, was studied using a xenon lamp (DPR, 1989). The xenon lamp had a spectral energy distribution similar to that of natural sunlight. The intensity of the lamp was measured with a radiometer (4.25 nm bandwidth) from 290 to 750 nm at 10-nm wavelength intervals. The study did not indicate if wavelengths less that 290 nm were filtered.   The degradation was found to be biphasic: an initial rapid rate of degradation, followed by a slower rate of degradation. The calculated photodegradation half-life of ^{14}C-methidathion for Phase 1 (Days 0-6) was equivalent to 8.96 days of natural sunlight. It took about 21.5 days of natural sunlight to complete Phase 2 (Days 6-17).   Under dark conditions similarly labeled methidathion showed a half-life of 123.9 days. No information was available whether the degradation under dark conditions was biphasic as well. Under aerobic conditions ^{14}C-methidathion degraded rapidly from a value of 90.3% (Day-0) of the applied radioactivity to 7.6% by Day 11, and was not detectable by day 145. The calculated first order half-life was 3.1 days (DPR, 1990). Under anaerobic conditions ^{14}C-methidation degraded, and declined from a mean of 41.4% on Day-0 (anaerobic incubation) to 2.0% on Day-30 and to 0.6% on Day-62. In sterile soil samples, ^{14}C-methidathion had a half-life of 35.5 days (DPR, 1990). This shows that the aerobic microbes are actively breaking down methidation under the experimental conditions used. However, in the absence of air (oxygen), or microbes as in sterile conditions, methidation may breakdown at slower rate.

Fate in Other Environments
Vorkamp et al., (2002) studied the fate of methidathion resides in biological waste during anaerobic digestion. They conducted three reactor experiments under various conditions

of temperature, pH, and retention time. The influence of pH and temperature as well as the partitioning between solid and aqueous phases were studied in batch experiments. The mesophilic reactor experiments (i.e. where the organisms favor a moderate temperature such as 25, 35 ^{0}C) showed a decline to about 10% of the maximum methidathion concentration within 30-80 days. In the thermophilic (organisms that favor a higher temperature like 55 ^{0}C) reactor experiment, methidathion disappeared within 20 days. The batch experiment showed an abiotic hydrolysis of methidathion over a period of 4 days, accelerated by alkaline conditions (pH 10.5 and 12.8) and high temperature (55 ^{0}C). The hydrolysis was also noticeable at a neutral pH, while methidathion was most stable at weakly acidic pH values. Methidathion bonded strongly to the biological waste, and the amount released into the water phase was below the maximum aqueous solubility. About 10 % of the methidathion remained non-extractable. They suspected co-sorption of methidathion to solid organic matter to be the reason. In a field soil dissipation study of methidathion, applied to alfalfa, in Fresno County, California, (DPR, 1986), the following was reported. The stability and mobility of methidathion and it's principal degredate [S-(2-methoxy-5-oxo-Δ^2 –1,3,4-thiadiazonil-4yl-methyl)-O,O-dimethyl-phosphorodithioate] in a Hanford fine sandy loam, when the pesticide was applied in a series of twelve applications, of 1.0 lb. a.i. per acre, the methidathion concentration in the first 0.6 inches of soil reached an average maximum value of 0.14 ppm; and the estimated initial soil half-life was eight days. The derivative was not found in any 0-6" or 6-12" soil cores. Although methidathion was detected in samples collected from a depth of 6-12" on the day of application, none was detected in any subsequent samples from this depth. This dissipation pattern suggests that the loss of methidathion in the 0-6" layer was not due to the downward migration of residues. The study concluded that when applied to an alfalfa stand in California, methidathion should not persist or accumulate in soil, and should not leach to lower soil depths.

Since methidathion is applied on many agricultural cops, it is important to examine whether this pesticide is detected in fruits, other commodities, including some processed products. Balaso et al., (2003) studying fifty samples of honey collected from local markets in Portugal and Spain during 2002, detected methidathion in 4% of the samples. In an investigation on degradation of pesticides that included methidathion in fortified red and white wine under conditions of light and darkness, Stavropoulos et al., (2001) followed their degradation for 80 days. They found that the half-life values of methidathion for white and red wine stored in diffuse daylight conditions were 20.1 and 20.0 days respectively. The half-lives in darkness were 21.1 and 24.2 days respectively. They concluded that photo-degradation does not play a role in decomposition of methidathion in wine under the study conditions. Kyriakidis et al., (2000) in a similar study investigated decomposition of methidathion sprayed on covered and uncovered grape vines. They sampled grapes 2 hours and 20 days after spraying, and stored either in a refrigerator, or left on the vine. They estimated the half-life of methidathion to be 5 days for uncovered vines and 7 days for covered vines, and 64 days for grapes stored in the refrigerator. Kyriakidis et al. in 2000, studied the effect of storage temperature and juice acidity on the degradation rate of methidathion in orange and peach juices. A known quantity of methidathion was added aseptically to these two juices and stored at

40, 15, and 0 ^{0}C, respectively. They found that refrigeration extended the half-life of methidathion beyond that of methidathion in the same juice samples stored at room temperature. The half-lives of methidathion in orange and peach fruit juices were; 330, and 385 days at 0 ^{0}C, 115 and 114 days at 15 ^{0}C, and 4.1 and 3.8 days, respectively, at 40 ^{0}C. A five-year monitoring survey was conducted in Japan (Akiyama et al., 2002) where they examined the presence of pesticide residues in a variety of agricultural products offered at the markets. They detected methidathion from local origin tomato, and from imported orange and grapefruit samples.

Fate and Persistence in the Atmosphere

When methidathion enters the atmosphere, it may be transformed through reactions with atmospheric radicals (OH and NO_3) and ozone (O_3). The potential for human exposure to methidathion and subsequent transformation products is therefore related to the rate of dispersion and potentially to the atmospheric lifetime and reaction rates for removal from the atmosphere. Although no data are available on the gas phase atmospheric chemistry of methidathion, literature data are available on the reactions of related organophosphorus compounds with O_3, OH, and NO_3. Studies conducted in environmental chambers have shown that atmospheric reactions of these compounds with O_3 and NO_3 are relatively unimportant. Reactions involving OH radicals, however, were found to be important with atmospheric lifetimes ranging from 0.8 hours to 2 days (Winer and Atkinson, 1990, Aschmann and Atkinson, 2006, and Tuazon et al, 2006). Goodman et al., (1988), and Aschmann and Atkinson, (2006) investigated the kinetics of the atmospherically important gas-phase reactions of a series of trimethyl phosphorothioates. One of the compounds studied; $(CH_3O)_2P(S)SCH_3$ is structurally similar to methidathion. For this compound they estimated a rate constant for reaction with OH radicals at room temperature of 5.5 x 10^{-11} cm^3 molecule $^{-1}$s^{-1} and a calculated lifetime due to reaction with OH radicals of 5.0 hr for a 12-hr average OH radical concentration of 2.0 x 10^6 molecule cm^{-3}. The Estimation Programs Interface (EPI) Suite™ is a Windows® based series of physical/chemical property and environmental fate estimation models developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation. AOPWIN™, an individual model in EPI Suite™, estimates the gas-phase reaction rate for the reaction between a chemical and OH, the most prevalent atmospheric oxidant (Meylan and Howard, 1993). The model also determines if NO_3 reaction will be important, and gas-phase O_3 reaction rates are estimated for olefins and acetylenes. Atmospheric half-lives are automatically calculated using assumed average OH and O_3 concentrations. AOPWIN™ used on methidathion resulted in an overall rate constant (k_{OH}) of 149.8 x 10^{-12} cm^3/molecule-sec, with a corresponding half-life of 0.071 day (12-hour day; 1.5 x 10^6 [OH]/cm^3). There were no structure matches in the model's experimental database. Atkinson et al., (1989), and Aschmann and Atkinson, (2006) examined the product formation from the gas-phase reactions of OH radicals with $(CH_3O)_3PS$, $(CH_3O)_2P(S)SCH_3$, $(C_2H_5O)2P(S)CH_3$, and $(C_2H_5O)_3PS$. When reacting with OH radicals in daylight, the P=S bonds were oxidized in part to P=O bond containing products commonly known as oxons.

Aston and Seiber (1997) investigated airborne levels of methidathion and other organophosphates in the Sierra Nevada Mountains. In this study, residues of methidathion, and its oxon were detected in air (Table 09) as well as on pine needle samples.

Table 09: Concentration of methidathion and methidaoxon in air at study sites in California during summer of 1994 (adapted from Aston and Seiber, 1997).

Compound	Laboratory Limits of Quantitation	Lindove elevation 114 meters.	Ash Mountain elevation 533 meters.	Kaweah elevation 1920 meters
	pg/m^3	pg/m^3 range	pg/m^3 range	pg/m^3 range
Methidathion	85	15,000-400	230-[a]NQ	NQ
Methidaoxon	170	10,000-280	660-210	210-[b]ND

[a] NQ- not quantified.
[b] ND– not detected, (minimum detection limit: MDL 170 pg/m^3)

They found relatively high levels of methidathion and it's oxon at the site closest to Lindcove, CA, located in the Central Valley. At higher elevations, ambient air contained lesser amounts of parent pesticide. The derivative oxon form was more frequent relative to parent methidathion form at higher elevations. Pine needles from lower elevations contained small but detectable amount of both forms, but only the oxon form was detected at mid elevation. None was detected at the high elevation. They deduced that for airborne methidathion, foliar deposition is a significant summer fate process, along with atmospheric degradation and dilution. No data was presented of deposition on soil or on any other open surface.

The Air Resources Board, State of California, contracted a methidathion ambient and application air monitoring study in 1991, at the request of the Department of Pesticide Regulation, (Royce et al, 1993). Both ambient and application monitoring for methidathion and its more toxic oxidation product, methidaoxon, were performed in Tulare County, during June and July of 1991. The reason that the monitoring was done in this county was due to high use of methidation on citrus crops. Both methidathion and methidaoxon were detected at all five ambient monitoring sites and during the application-monitoring period. The site named as Exeter Union High School, Exeter, in the study (Royce et al, 1993) should be corrected as Kaweah High School.

From Table10 and Table11, it is evident that both methidathion and methidaoxon were detected in ambient air at these sites during the study period. The maximum positive methidathion detection during this monitoring ranged from 0.07 $\mu g/m^3$ (5.6 ppt) to 0.56 $\mu g/m^3$ (45.2 ppt). More than 91 % of the total samples analyzed had no detectable residues (minimum detection limit = 0.03 $\mu g/m^3$; (2.42 ppt) for a 24 hour sample). The maximum detection for methidaoxons ranged from 0.092 $\mu g/m^3$ (7.42 ppt) to 0.10 $\mu g/m^3$

(8.87 ppt). Over 97 % of the total samples analyzed had no detectable residues (minimum detection limit = 0.09 μg/m^3; (7.26 ppt) for 24 hour sample).

Application monitoring for methidathion and methidaoxon was conducted in July 1991, for 48 hours after an application, in Tulare County (Tables 12 & 13). Methidathion was applied by ground equipment at a rate of 1.5 pounds of a.i. per acre. Three sites were monitored. The samplers were situated approximately 25 yards north, 15 yards southeast, and 150 yards southeast of a 15 acre orange grove that received the methidathion application. Maximum positive methidathion detection from all sites ranged from 0.28 μg/m^3 (22.6 ppt) to 3.16 μg/m^3 (255 ppt). Almost 48 percent of the total samples analyzed had no detectable residues (minimum detection limit = 0.03 μg/m^3 (2.42 ppt) for a 24 hour sample). Maximum positive methidaoxon detections at each site ranged from 0.33 μg/m^3 (28.1 ppt) to 0.36 μg/m^3 (30.7 ppt). More than 76 percent of the total number of samples analyzed had no detectable residues (minimum detection limit = 0.09 μg/m^3 (7.26 ppt) for a 24 hour sample).

Table 10.   Summary of methidathion ambient air monitoring results in Tulare County. Samples (24-hour) were taken over a four-week period from June 27 to July 25, 1991. The Air monitoring station in Visalia was the background site (Royce et al., 1993).

Monitoring Site	Highest [a]$\mu g/m^3$	Positive [b]ppt	2nd Highest $\mu g/m^3$	Positive ppt	Mean Positive[c] $\mu g/m^3$	ppt	# of Samples[d]	# Above [e]EQL
Sunnyside Union School, Strathmore	<EQL	<EQL	<EQL	<EQL	[f]NA	NA	17	0
Jefferson School, Lindsay	0.56	45.2	0.30	24.2	0.16	12.9	17	6
Kaweah High School	0.07	5.64	<EQL	<EQL	0.07	5.64	15	1
U.C. Lindcove Field Station, Exeter	<EQL	<EQL	<EQL	<EQL	NA	NA	15	0
Visalia	<EQL	<EQ	<EQ	<EQ	NA	NA	17	0
						Total	**81**	**7**

[a]micrograms per cubic meter

[b]parts per trillion

[c]mean of samples above the EQL

[d]field blanks and collocated samples excluded

[e]Estimated Quantitation Limit = 0.03 $\mu g/m^3$ (2.42 ppt) for a 24-hour sample

[f]Not Applicable

Table 11. Summary of methidaoxon ambient air monitoring results in Tulare County. Samples (24-hour) were taken over a four-week period from June 27 through July 25, 1991. The Air monitoring station in Visalia was the background site (Royce et al, 1993) (adjusted to account for background values).

Monitoring Site	**Highest** [a]μg/m³	**Positive** [b]ppt	**2nd Highest** μg/m³	**Positive** ppt	**Mean** μg/m³	**Positive**[c] ppt	**# Samples**[d]	**# Above** [e]EQL
Sunnyside Union School, Strathmore	0.069	5.89	<EQL	<EQL	0.069	5.89	17	1
Jefferson School, Lindsay	0.077	6.58	<EQL	<EQL	0.097	8.29	17	3
Kaweah High School	<EQL	<EQL	<EQL	<EQL	[f]NA	NA	15	0
U.C. Lindcove Field Station, Exeter	<EQL	<EQL	<EQL	<EQL	NA	NA	15	0
Visalia	<EQL	<EQL	<EQL	<EQL	NA	NA	17	0
						Total	**81**	**4**

[a]micrograms per cubic meter

[b]parts per trillion

[c]mean of samples above the EQL

[d]field blanks and collocated samples excluded

[e]Estimated Quantitation Limit = 0.09 μg/m³ (7.26 ppt) for a 24-hour sample

[f]Not Applicable

Table 12.   Summary of air monitoring results after an application of methidathion to an orange orchard (1.5 pounds of active ingredient per acre application rate). Samples were collected in Tulare County during July 1991 before, during and for 48 hours after application (Royce et al., 1993).

| | ^{a}µg/m^3 (ppt) | | | | | | | |
| | | | | Sampling | Interval^b | | | Maximum |
Site	1	2	3	4	5	6	7	Positive
North	<EQL^c (<EQL)	0.33 (26.6)	0.86 (69.3)	1.40 (113)	0.82 (66.1)	3.16 (255)	0.46 (37.1)	3.16 (255)
Southeast-1	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	1.25 (101)	0.60 (48.4)	0.30 (24.2)	1.25 (101)
Southeast-2	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.28 (22.6)	0.10 (8.06)	<EQL (<EQL)	0.28 (22.6)
Maximum Positive	<EQL (<EQL)	0.33 (26.6)	0.86 (69.3)	1.40 (113)	1.25 (101)	3.16 (255)	0.46 (37.1)	3.16 (255)

^{a}microgram per cubic meter and (parts per trillion)

^{b} interval 1 =background on 7/10/91 from 1500-1600; interval 2 =during application on 7/10-11/91 from 2330-0900; interval 3 = 7/11/91 from 0900-1100; interval 4 = 7/11/91 from 1100-1500; interval 5 = 7/11/91 from 1500-2130; interval 6= 7/11-12/91 from 2130-0730; interval 7= 7/11-12/91 from 0730-0730;

^{c} Estimated Quantitation Limit = 0.03 µg/m^3 (2.42 ppt) for a 24-hour sample

Table 13. Summary of air monitoring results for methidaoxon after an application of methidathion to an orange orchard (1.5 pounds of active ingredient per acre application rate). Samples were collected in Tulare County during July 1991 before, during and for up to 48 hours after application (Royce et al., 1993) (adjusted to account for background values).

	[a]μg/m^3 (ppt)							
				Sampling	Interval[b]			Maximum
Site	1	2	3	4	5	6	7	Positive
North	<EQL[c] (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.31 (26.5)	0.24 (20.5)	0.21 (17.9)	0.31 (26.5)
Southeast-1	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.34 (29)	<EQL (<EQL)	0.13 (11.1)	0.34 (29)
Southeast-2	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)
Maximum Positive	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	<EQL (<EQL)	0.34 (29)	0.24 (20.5)	0.21 (17.9)	0.34 (29)

[a]micrograms per cubic meter and (parts per trillion)

[b] interval 1 =background on 7/10/91 from 1500-1600; interval 2 =during application on 7/10-11/91 from 2330-0900; interval 3 = 7/11/91 from 0900-1100; interval 4 = 7/11/91 from 1100-1500; interval 5 = 7/11/91 from 1500-2130; interval 6= 7/11-12/91 from 2130-0730; interval 7= 7/11-12/91 from 0730-0730;

[c] Estimated Quantitation Limit = 0.09 μg/m^3 (7.26 ppt) for a 24-hour sample

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